

Environmental effects on electronic excitation energy transfer in organic liquid scintillators

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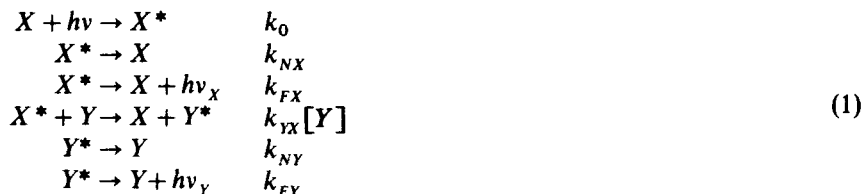
Abstract. The efficiency of electronic excitation energy transfer from toluene to a dissolved fluorescent indole, is determined experimentally in systems comprising neat toluene, 1:9 mixture of toluene-cyclohexane and 1:9 mixture of toluene-paraffin as a function of temperature in the range 293–353°K (viscosity range 0.6–39 cP). The results are discussed in terms of the influence of temperature, dilution and viscosity of the medium on the energy transfer efficiency in binary organic scintillator systems.

Keywords. Energy transfer; organic liquid scintillators; fluorescence.

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1. Introduction

It is known (Lumb 1978; Brooks 1979) that when a solvent molecule in a binary organic liquid scintillator system is excited to its first pi-electronic singlet state, the excitation energy from this state of the solvent molecule is transferred to a solute molecule non-radiatively and this eventually results in the fluorescence emission from the solute molecule. The relevant photophysical processes that occur following the excitation of the solvent molecules (X) to the subsequent emission of fluorescence by the solute molecules (Y) may be represented as



where $h\nu$ denotes a photon, an asterisk the excited state of a molecule and ks the probabilities per unit time (or the rate constants) for the corresponding processes; here $[Y]$ represents the solute concentration in the system. The transfer of energy from an excited solvent molecule to an unexcited solute molecule in a scintillator system is supposed to take place when the two interacting molecules come sufficiently close to each other as a result of molecular diffusion and excitation energy migration among the solvent molecules. Obviously the material diffusion of the molecules depends on the temperature and viscosity, and the energy migration from an excited solvent molecule

to a neighbouring unexcited solvent molecule on the degree of dilution of the solvent medium. Though some studies on the individual effects of temperature, viscosity and dilution on the energy transfer efficiency of some organic scintillator systems have been made (Laustriat and Coche 1960; Elkana *et al* 1968; Levin *et al* 1971; Chalzel 1977), there has been no systematic study of the effects of all these factors on the energy transfer efficiency of any single scintillator system so far.

In view of this we studied the efficiency f_{TX} of energy transfer from toluene to 1-*p*-chlorophenyl-5-benzyloxy-2-phenylindole as a function of temperature in three types of systems, neat toluene (TN), 1:9 mixture of toluene and cyclohexane (TC) and 1:9 mixture of toluene and liquid paraffin (TP). Toluene is commonly used as a scintillator solvent and indole is known (Basavarajappa *et al* 1982) to be a good scintillator. Cyclohexane is a neutral diluent having a viscosity comparable to that of toluene and liquid paraffin is also a neutral diluent but has a much higher viscosity. The presence of cyclohexane in TC system is expected to influence only excitation energy migration because an excited solvent molecule in this system is surrounded by a large number of neutral diluent molecules; and that of liquid paraffin in TP system to influence both excitation migration and diffusion processes, thus affecting to different degrees the energy transfer efficiency of these scintillator systems.

2. Experimental

All the chemicals used in the present studies were obtained from commercial firms and were of spectral grade. The indole (synthesized) was of sufficiently high purity. The scintillator concentration was chosen to be 1 g/l in all the systems.

Energy transfer efficiency was measured by the method of Cohen and Weinreb (1956). In this method the solute fluorescence intensity is measured under the successive excitation of the solvent (*X*) and the solute (*Y*) by using uv radiation of appropriate energy to excite these molecules. The experimental arrangement is shown schematically in figure 1. uv radiation from a 400 W mercury lamp (S) was dispersed in a Bausch and Lomb monochromator (MC) and the radiation of selected wavelength was focussed using a quartz lens (L) onto a quartz cell (C) containing the scintillator solution. The cell was placed in a Beckman temperature regulated cell holder (H). A Barr and Stroud UMS graded narrowband filter (F) was placed at the exit slit of the monochromator to avoid any stray radiation entering the solution. A photomultiplier (PM) GEC 931A,

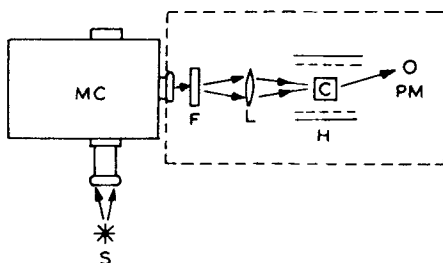


Figure 1. Schematic diagram of the experimental arrangement for determination of energy transfer efficiency. (S, uv source; MC monochromator; F, narrowband filter; L, quartz lens; C, quartz cell; H, temperature regulated cell holder; PM, photomultiplier.)

placed slightly off the direction of the incident radiation, was used to detect the fluorescence intensity and the photomultiplier output current was measured by a Keithley (610 C) electrometer. Prior to the fluorescence measurement, pure and dry nitrogen was passed through the solution to expel the dissolved oxygen which quenches the fluorescence intensity and the cell was hermetically stoppered in the inert nitrogen atmosphere.

Radiation of wavelengths 265 and 302 nm respectively were used for excitation of the solvent and the solute molecules. In the experiment, when only the solute molecules are excited by absorption of n_1 number of incident quanta, the observed solute fluorescence intensity (I_1) is

$$I_1 = An_1\phi_Y \quad (2)$$

where A is a constant depending upon the experimental arrangement and ϕ_Y is the quantum yield of the solute molecules. When only the solvent molecules are excited by absorption of n_2 number of incident quanta, a fraction f_{YX} of the excited solvent molecules transfer their excitation energy to the solute molecules and the observed solute fluorescence intensity (I_2) is

$$I_2 = An_2f_{YX}\phi_Y \quad (3)$$

I_1 and I_2 was measured and the ratio n_2/n_1 was estimated by comparing the fluorescence intensities of an aqueous solution of fluorescein sodium whose quantum efficiency is constant under both the excitation wavelengths. The values of f_{YX} thus evaluated at different temperatures using (1) and (2) are given in table 1 for all the three systems.

The viscosities of TN and the mixtures TC, and TP were measured using standard Ostwald viscometers of appropriate ranges and a temperature regulated water bath whose temperature (T) could be controlled within an accuracy of 0.01°C. The values of viscosity (η) are also included in table 1.

3. Results and discussion

It is observed (table 1) that apart from a slight initial increase in its value the energy transfer efficiency f_{YX} decreases with increase in temperature in all the scintillator

Table 1. Values of energy transfer efficiency f_{YX} and viscosity η for TN, TC and TP systems at different temperatures.

System T (K)	TN		TC		TP	
	η (cP)	f_{YX}	η (cP)	f_{YX}	η (cP)	f_{YX}
293	0.61	0.62	0.86	0.58	39.0	0.52
303	0.54	0.63	0.73	0.60	26.0	0.54
313	0.48	0.62	0.62	0.59	17.0	0.54
323	0.43	0.61	0.53	0.58	12.0	0.52
333	0.39	0.60	0.47	0.56	8.7	0.52
343	0.35	0.58	0.40	0.55	6.4	0.50
353	0.32	0.56	0.36	0.53	4.7	0.48

systems. For a temperature change of about 17% in the present study the decrease in f_{YX} on the average is 9% in all the systems. It is interesting to note that although f_{YX} decreases at each of the temperatures from TN to TC to TP system, the changes in its value are not significant as compared to the remarkably large changes in dilution and viscosity of the medium among these systems. The dilution in TC system as compared to TN is as much as 90% while the decrease in f_{YX} from TN to TC system at each of the temperatures is about 5%. The increase in viscosity from TC to TP system is about 45 times at 293°K and about 13 times at 353°K but the decrease in f_{YX} at both the temperatures is nearly the same (about 10%). The maximum change in viscosity from TN system at 353°K to TP at 293°K is as large as 120 times but the change in f_{YX} is only about 7%. Thus the behaviour of f_{YX} with regard to changes in temperature, dilution, and viscosity of the medium in these systems may appear very strange but can be understood on the following considerations.

It can be seen from the kinetic scheme (1) that the efficiency f_{YX} which is the probability that an excited solvent molecule transfers its energy to a solute molecule at any given solute concentration $[Y]$ may be basically expressed as

$$f_{YX} = k_{YX}[Y]/(k_{YX}[Y] + k_{NX}) \quad (4)$$

where k_{YX} is the probability per unit time of de-excitation of a solvent molecule by energy transfer to a solute molecule and k_{NX} is that due to other (non-energy transfer) processes. Thus we see that the energy transfer efficiency is essentially governed by the probabilities k_{YX} and k_{NX} . For the solute concentration of 1 g/l of our systems we may write (4) as

$$(f_{YX}^{-1} - 1)^{-1} = k_{YX}/k_{NX} \quad (5)$$

The variation of the estimated values of k_{YX}/k_{NX} with temperature for all the three systems is shown in figure 2. It is fruitful to note that in spite of considerable changes in dilution and viscosity of the medium, the ratio k_{YX}/k_{NX} is the same at 333° and 353°K between TN and TC systems and between TC and TP systems. This is obvious if we consider the way in which temperature, dilution, and viscosity of the medium affect the parameters k_{YX} and k_{NX} . The probability k_{YX} of de-excitation of the solvent molecules by

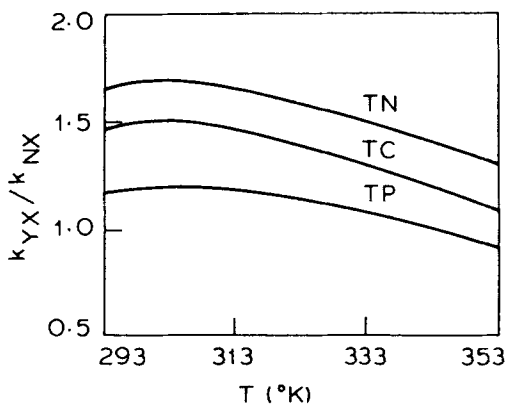


Figure 2. Variation of k_{YX}/k_{NX} with temperature for TN, TC and TP systems.

energy transfer to solute molecules may increase with temperature for all the systems due to increase in solvent-solute encounters and k_{NX} may also increase with temperature due to increase in the solvent-solvent encounters. Whereas k_{YX} may decrease with increase in dilution and viscosity of the medium due to decrease in the probability of a solvent-solute encounter, k_{NX} may also decrease likewise due to decrease in the probability of a solvent-solvent encounter. Thus, we see that any apparent changes in f_{YX} due to changes in temperature, dilution and viscosity of the medium, to a large extent, are offset by similar changes in k_{YX} and k_{NX} . Indeed, failure to appreciate this result may even lead to erroneous conclusions as to the influence of temperature, dilution and viscosity of the medium on the energy transfer process. It may be stated that a knowledge of the exact changes in the probability k_{NX} , and hence k_{YX} , due to changes in temperature, dilution and viscosity of the medium is essential for a precise understanding of the effect of these various environmental factors on the energy transfer process in liquid scintillators.

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